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Redetermination of bis(2-aminopyrimidine)-bis(nitrato)copper(II)

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Key indicators

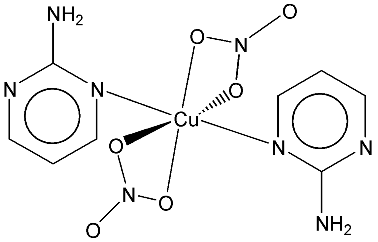
Single-crystal X-ray study
T = 193 K
Mean σ(C–C) = 0.004 Å
R factor = 0.034
wR factor = 0.100
Data-to-parameter ratio = 11.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The crystal structure of the title compound, $[Cu(NO_3)_2(C_4H_5N_3)]$, at room temperature was reported earlier, but full results were not published. According to the present study at 193 K, the Cu^{II} atom occupies a special position at an inversion centre and has a distorted octahedral geometry. The basal plane is formed by two N atoms of two 2-aminopyrimidine molecules and two O atoms of two *trans*-oriented nitrate anions. The apical positions are occupied by the remaining O atoms of the chelating nitrate groups. The hydrogen bond, formed by an amino group and the uncoordinated pyrimidine N atom of a 2-aminopyrimidine ligand of the neighbouring molecule of the complex, gives rise to Watson–Crick-type pairwise aggregation of amino-pyrimidine ligands, thus creating infinite chains of molecules of the complex stretching along the $[10\overline{1}]$ direction in the crystal. The chains are further interconnected into layers parallel to the $x0z$ plane, due to additional hydrogen bonds involving the second H atom of the amino group of the 2-aminopyrimidine ligand and the O atom of the nitrate anion of the neighbouring molecule.

Comment

The ligand used in this study, 2-aminopyrimidine (abbreviated as ampym), attracts attention due to its ability to form strong hydrogen-bonded pairs of the Watson–Crick-type (van Albada, Quiroz-Castro *et al.*, 2000; van Albada, Smeets *et al.*, 2000). In the known structures of Cu^{II} compounds with the ampym ligand, it acts as either a mono-chelating (Lumme *et al.*, 1996; O'Reilly *et al.*, 1983, 1984; Kennard *et al.*, 1985; Mak *et al.*, 1987; Pon *et al.*, 1997) or a bis-chelating ligand in polymeric structures (Smith *et al.*, 1985; Lynch & Duckhouse, 2000). With strong anions, such as Cl$^-$ and Br$^-$, infinite chains are formed with either protonated or diprotonated amino-pyrimidine as cations (Pon *et al.*, 1997; Zanchini & Willett, 1990; Manfredini *et al.*, 1990). Recently, a dihydroxy-bridged dinuclear Cu^{II} compound with this ligand was studied (van Albada *et al.*, 2001).



(I)

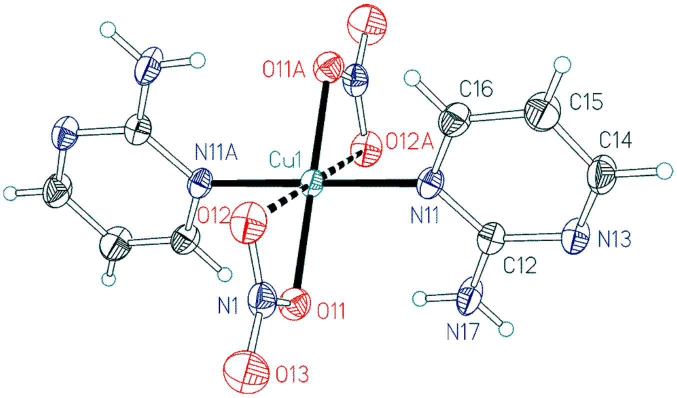


Figure 1
The structure of the title compound with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

In a preliminary study, the X-ray structure of the title compound, (I), was determined at room temperature (Lumme *et al.*, 1981), but as neither atomic coordinates, nor details of the experiment were published, we redetermined this structure. The Cu^{II} atom occupies a special position at an inversion centre and has a distorted octahedral coordination (Fig. 1). The basal plane is formed by two N atoms of two ampym ligands (N11 and N11*A*) with a Cu—N11 distance of 1.989 (2) Å and two O atoms of two *trans*-oriented nitrate anions (O11 and O11*A*) with a Cu—O11 distance of 1.9965 (19) Å. The apical positions are occupied by the remaining O atoms of the nitrate groups (O12 and O12*A*) with a Cu—O12 distance of 2.459 (2) Å. This is in agreement with distances found in the literature for dicoordinating *trans*-oriented nitrate anions (Diefenbach *et al.*, 1996; Cameron *et al.*, 1972; Lewis & Hodgson, 1973; Neenan *et al.*, 1996).

The lattice is stabilized by stacking of the pyrimidine rings with an interplanar distance of 3.897 Å and by a hydrogen-bonding system (Watson–Crick-type) between the amino N17 atoms and the uncoordinated pyrimidine N13 atom of a neighbouring ampym ligand [H17*A*$\cdots$N13^{i} 2.12 Å, N17—H17*A*$\cdots$N13^{i} 143 Å and N17$\cdots$N13^{i} 2.976 (3) Å; symmetry code: (i) $2-x$, $1-y$, $1-z$], forming linked pairs of ampym ligands and thus connecting the molecules of the complex into infinite chains along the $[10\overline{1}]$ direction (Fig. 2). The same hydrogen-bonding pattern was reported earlier in the structures of complexes of the ampym ligand (van Albada, Quiroz-Castro *et al.*, 2000; van Albada, Smeets *et al.*, 2000). The above-mentioned chains in the structure of the title compound are further interconnected into layers parallel to the $x0z$ plane *via* additional hydrogen bonds involving the second H atom of the amino group of the ampym ligand and the O atom of the nitrate anion of the neighbouring molecule [N17*B*$\cdots$O12^{ii} 2.350 Å, N17—H17*B*$\cdots$O12^{ii} 137° and N17$\cdots$O12^{ii} 3.037 (3) Å; symmetry code: (ii) $1+x$, y, z]. The H17*B* atom is also involved in the intramolecular hydrogen bond N17—H17*B*$\cdots$O11 [H17*B*$\cdots$O11 2.486 Å, N17—H17*B*$\cdots$O11 122° and N17$\cdots$O11 3.026 (3) Å].

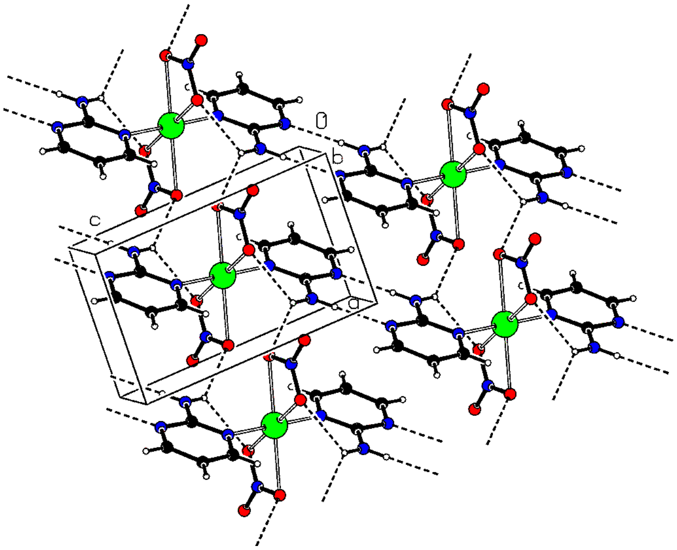


Figure 2
A fragment of the hydrogen-bond system in the crystal of the title compound.

In the IR spectrum of the title compound, one strong and one somewhat weaker vibration are present at 3446 and 3333 cm^{-1}, which can be attributed to the hydrogen bonds. The vibrations of the coordinating nitrate anions, in agreement with the literature (Neenan *et al.*, 1996), are observed at 1499, 1274 and 1018 cm^{-1}.

The ligand-field spectrum, measured from a solid with the diffuse-reflectance technique, shows a band at 17.5×10^{3} cm^{-1} with a shoulder at 14.0×10^{3} cm^{-1}, which is a normal ligand-field transition for a CuN_2O_2 or a $CuN_2O_2(O)_x$ chromophore (Hathaway, 1987; Amani Komaei *et al.*, 1998, 1999). The EPR, measured on a polycrystalline powder at room temperature, shows an axial $S = 1/2$ spectrum with a $g_{\perp}$ of 2.08 and a broad $g_{\parallel}$ of 2.25, typical for a mononuclear Cu^{II} compound.

Experimental

The ampym ligand was obtained commercially and used without purification. The compound was obtained by adding 0.2 *M* ampym, dissolved in ethanol, to a solution of 0.1 *M* copper(II) nitrate in ethanol. Use of methanol gave the same result. Upon standing in air blue crystals were formed. Yield 82%. Elemental analysis [found (calculated)] for $C_8H_{10}CuN_8O_6$: 25.5 (25.4)% C; 2.5 (2.7)% H; 29.6 (29.7)% N. A crystal was selected for the X-ray measurements and mounted on a glass fibre using the oil-drop method (Kottke & Stalke, 1993)

Crystal data

$[Cu(NO_3)_2(C_4H_5N_3)]$
$M_r = 377.78$
Triclinic, $P\overline{1}$
$a = 5.691$ (1) Å
$b = 7.091$ (2) Å
$c = 8.983$ (2) Å
$\alpha = 81.02$ (3)°
$\beta = 81.46$ (3)°
$\gamma = 69.51$ (3)°
$V = 333.68$ (13) Å^3

$Z = 1$
$D_x = 1.880$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 12$–27°
$\mu = 2.82$ mm^{-1}
$T = 193$ (2) K
Plate, purple
$0.50 \times 0.20 \times 0.06$ mm

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Data collection

Enraf-nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.580$, $T_{\max} = 0.844$
2565 measured reflections
1177 independent reflections
1164 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.042$
$\theta_{\max} = 66.9°$
$h = -6 \rightarrow 6$
$k = -8 \rightarrow 8$
$l = -10 \rightarrow 10$
3 standard reflections every 200 reflections intensity decay: 2.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.100$
$S = 0.81$
1177 reflections
106 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0864P)^2 + 0.6111P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.59$ e Å^{-3}
$\Delta\rho_{\min} = -0.51$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—N11	1.989 (2)	Cu1—O12	2.459 (2)
Cu1—O11	1.9965 (19)		
N11—Cu1—O11	90.57 (8)	N11—Cu1—O12	90.37 (2)

The H atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms. Their $U_{\rm iso}$ were constrained to be $1.2U_{\rm eq}$ of the carrier atom.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1985); cell refinement: *CAD*-4 *Software*; data reduction: *XCAD*4 (Harms, 1996); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL-PC* (Sheldrick, 1995); software used to prepare material for publication: *SHELXL*97.

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